Determination of trace anions in organic solvents

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Abstract

Ion chromatography along with matrix elimination was used to reliably determine trace levels of anionic contaminants in organic solvents. A 5-ml sample volume was injected directly into the instrument without any sample pretreatment. High-purity deionized water was used to deliver the sample to a preconcentration column, where the anions of interest were retained while the organic matrix was rinsed to waste. A sodium carbonate eluent eluted concentrated anions from the preconcentration column and separated them on a 2-mm pellicular anion-exchange column. The separated anions were detected by suppressed conductivity. This method was used to determine the anionic contaminants of isopropanol, acetone and *N*-methylpyrrolidone. Method detection limits for chloride, nitrate, sulfate and phosphate were all lower than 1 μg/l. © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

In the manufacture of semiconductor materials, a great deal of attention is focused on minimizing sources of contamination. Yield and reliability can be significantly compromised by ionic contamination [1]. Of particular interest are those chemicals that come into contact with micro-electronic circuitry, such as isopropanol (IPA), acetone and *N*-methylpyrrolidone.

Analysis of trace anions in solvents by wet chemical methods is laborious and time consuming. Procedures involve evaporation of a large volume of sample for several hours on a hot plate [2,3]. Anions are determined by either colorimetric or turbidimetric methods, and each anion must be determined separately. These techniques lack the sensitivity to detect trace concentrations (μg/l) as required by the semiconductor industry.

In a previous study, Kaiser and Wojtusik demonstrated the use of ion chromatography (IC) to determine trace anions in isopropanol [4]. Samples were analyzed without dilution or any other sample pretreatment. Method detection limits (MDLs) between 0.2 and 1.0 μg/l were achieved for chloride, sulfate, phosphate and nitrate. In another study, Sanders used this same approach and applied it to trace cation determination in water-immiscible organic solvents [5]. The use of solvent-compatible ion-exchange columns made both of these analyses possible [6].

This present study expands upon these works by optimizing the chromatographic conditions and considering other water-miscible organic solvents. The

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goals of this investigation were to reduce run time, enhance the chromatographic separation, and lower the method detection limits. A recently developed high-capacity ion-exchange column [7] with an isocratic carbonate-based eluent was evaluated for the preconcentration and separation steps of the analysis of IPA. Two other water-miscible organic solvents were analyzed: acetone and *N*-methylpyrrolidone.

2. Experimental

2.1. Chromatographic system

All chromatography was performed on a Dionex (Sunnyvale, CA, USA) DX-500 ion chromatograph. The system consists of a gradient pump (GP40), a conductivity detector (CD20), a liquid chromatography module (LC20) and a thermally stabilized conductivity detector (DS3). For sample loading, a Rheodyne (Cotati, CA, USA) six-port 9126-038 valve was fitted with a 5-ml loop made from 0.030 in. I.D. (0.75 mm) polyether ether ketone (PEEK) tubing. To preconcentrate the sample, another Rheodyne valve was used. A Dionex DXP single piston pump was used for pumping the deionized water rinse solution through the sample loop. A pressurizable reservoir chamber (Dionex) large enough to accommodate the sample container was maintained at 8 p.s.i. (55 kPa) with helium to fill the sample loop with sample.

All columns used in this study were manufactured by Dionex. The separations were performed on an IonPac AS9-HC analytical column (250×2 mm) and an IonPac AG9-HC guard column (50×2 mm). To concentrate the anions and eliminate the sample matrix, an IonPac AG9-HC concentrator column (50×4 mm) was used. The column and suppressor in the IC system were connected with 0.005 in. I.D. (0.125 mm) PEEK tubing. The lengths of the connecting tubing were kept as short as possible to minimize system void volume and ensure efficient 2-mm column operation. Care was taken to evenly cut tubing ends to avoid introducing any unwanted void volume.

The packing material for these anion-exchange columns is a macroporous resin with 2000 Å pores.

The resin consists of polyethylvinylbenzene cross-linked with 55% divinylbenzene. To this substrate, a layer of latex particle beads is permanently attached. An eluent of 8.0 mM sodium carbonate–1.5 mM sodium hydroxide was used to elute the analyte anions from the AG9-HC column set. An anion self-regenerating suppressor (ASRS) from Dionex was used to reduce the conductivity of the eluent [8]. The ASRS was operated in the external water mode to lower the level of the baseline noise [9].

To prevent contamination of the sample with anionic impurities in the rinse solution, an anion trap column (ATC-1) was used. This column contains a high-capacity anion-exchange resin in the hydroxide form. The ATC-1 was initially prepared for use by flushing (2 ml/min) with 200 ml of 200 mM sodium hydroxide followed by 100 ml of deionized water at the same flow-rate. The ATC was periodically regenerated using this procedure. The chromatographic conditions and pump program are listed in Tables 1 and 2, respectively.

2.2. Chemicals, solutions and samples

Reagent grade chemicals were used for standard and eluent preparation. The following samples of semiconductor grade reagents were analyzed: isopropanol (Pacific Pan, Hollister, CA, USA) and acetone (Olin Hunt Specialty Products, West Patterson, NJ, USA) and *N*-methylpyrrolidone (Ashland, Columbus, OH, USA).

Sodium hydroxide, 50% (w/w) from Fisher Scientific, (Pittsburgh, PA, USA) and a 0.5 M sodium carbonate eluent concentrate (Dionex) were used to prepare eluent. Deionized water with a specific resistance of 17.8 MΩ cm or greater from a Labconco (Kansas City, MO, USA) Water Pro PS water purification system was used to prepare all eluents, reagents, standards and the rinse solution.

Anion standards (1000 mg/l) for chloride, sulfate, phosphate and nitrate were prepared from the sodium and potassium salts obtained from Fisher Scientific. The salts were dried in a desiccator prior to weighing. Working standards were prepared by further diluting the 1000 mg/l standards to the range expected for the anions of interest. Dilute working standards were prepared weekly.

Table 1
Chromatographic conditions

Guard column	IonPac AG9-HC (50×2 mm)
Analytical column	IonPac AS9-HC (250×2 mm)
Preconcentrator column	IonPac AG9-HC (50×4 mm)
Trap column	ATC-1 anion trap column (4 mm)
Eluent	8.0 mM sodium carbonate–1.5 mM sodium hydroxide
Eluent flow-rate	0.25 ml/min
Rinsing reagent	Deionized water
Rinsing flow-rate	2.0 ml/min
Sample volume	5.0 ml
Detection	Suppressed conductivity, ASRS-ULTRA, AutoSuppression external water mode
ASRS current setting	100 mA

Table 2
Pump program (0=load or Off; 1=inject or On)

Time (min)	E1 (%)	Inject	Column	Relay 1 (pump)	Relay 2 (sample valve)	Remarks
Initial	100	0	0	0	0	Preconcentrator column in-line
0.00	100	0	1	0	0	Preconcentrator column out of line
0.10	100	0	1	1	0	DXP pump ON
4.90	100	0	1	0	0	DXP pump OFF
5.00	100	1	0	0	1	Inject, load loop
35.00	100	1	0	0	1	
35.01	100	0	0	0	1	

2.3. System operation

Trace anion analysis of solvents was accomplished in four steps: (1) filling the sample loop, (2) loading the concentrator, (3) eliminating the solvent matrix and (4) eluting the retained ions. Figs. 1–3 illustrate how the system performed these tasks. First, the sample was loaded into the 5-ml sample loop. A pressure of approximately 8 p.s.i. (55 kPa) was applied to the sample reservoir to ensure that the
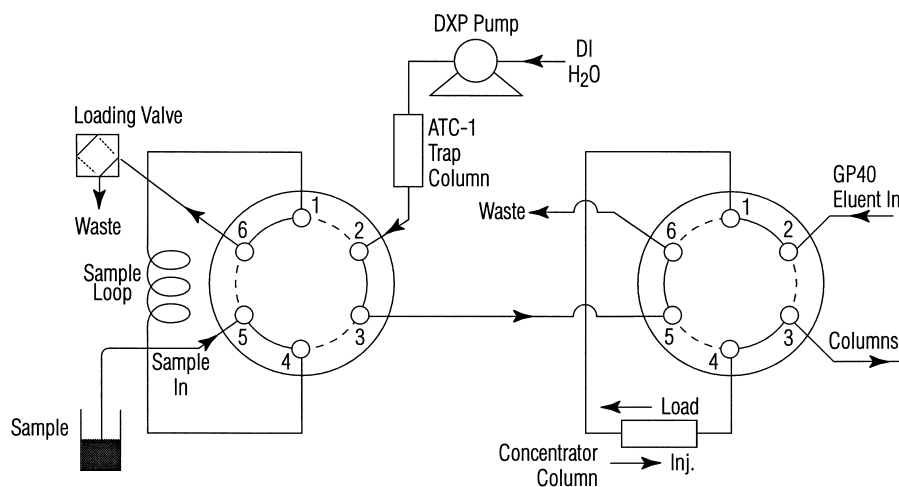

Fig. 1. IC matrix elimination instrument configuration: loading the sample loop.
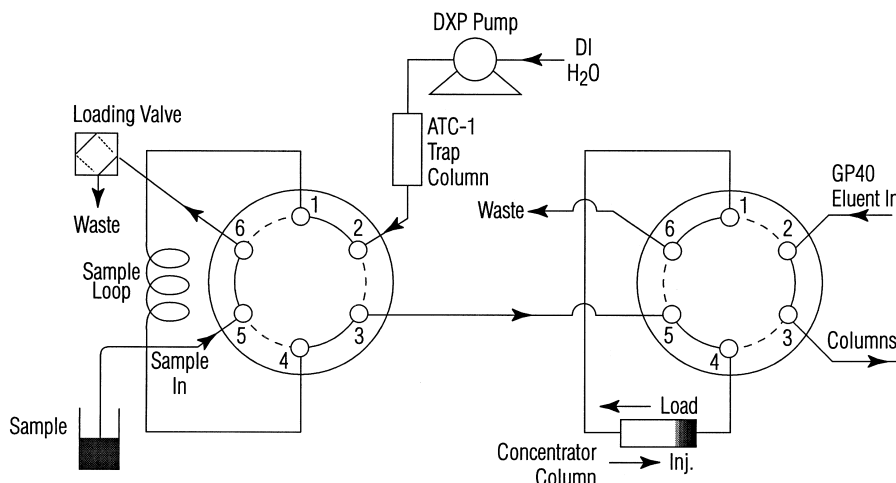
Fig. 2. IC matrix elimination instrument configuration: eliminating the matrix.

sample loop was consistently filled without bubbles (Fig. 1). To ensure that the loop contained a representative sample, at least four loop volumes (4×5 ml $= 20$ ml) were passed through the sample loop [10]. After the sample loop had been filled, deionized water pushed the sample out of the loop and onto the concentrator column in the opposite direction of the eluent flow (Fig. 2). Anions were retained on the concentrator column and the solvent matrix was eliminated by washing the IonPac AG9-HC concentrator column with deionized water at 2 ml/min. This step required 5 min and used 10 ml of deionized

water. Finally, by activating the "column" valve on the GP40, the concentrator column was switched in-line with the eluent stream and the analytical columns (Fig. 3). The anions were eluted from the concentrator column and separated on the analytical column set.

Special care was taken when performing trace analysis to minimize contamination. The deionized water used for preparing rinse solution, eluent and standards was free of measurable levels of ionic impurities, organics and particulate matter (larger than 0.2 μm). Any ionic contamination present in the
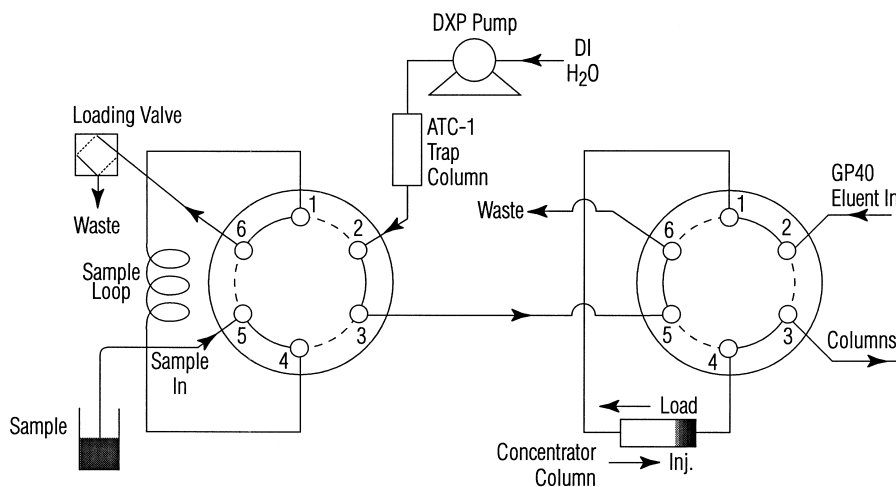

Fig. 3. IC matrix elimination instrument configuration: chromatographing the retained ions.

deionized water will be magnified in proportion to the volume needed for the rinsing step. To ensure the quality of the rinse water, the ATC-1 was periodically regenerated using the procedure described in Section 2.1. Success of this method was dependent on maintaining a consistent flow-rate for the DXP sample loading pump. Polyethylene sample containers were soaked for at least 24 h with 17.8 MΩ cm deionized water and rinsed several times prior to use. Disposable gloves (for electronics cleanroom applications) were worn at all times when handling apparatus that made contact with standard or sample.

A 5-ml sample loop was constructed from 0.03 in. (0.75 mm) I.D. PEEK tubing [432 in. (1097 cm) long]. Organic solvent samples were directly injected into the sample loop without dilution. A pressurized reagent reservoir was used for sample loading. This technique uses an inert gas to push sample from a sample container into the sample loop [11].

3. Results and discussion

The microbore format was chosen for the analytical columns and suppressor because it has several advantages [12]. There is a four-fold increase in mass sensitivity for the microbore (2 mm) over the standard bore microbore (4 mm) format with no loss in concentration sensitivity. Thus, smaller amounts of sample were required. This facilitated more convenient and faster loop loading. The microbore format also offered lower eluent consumption, as well as less eluent waste.

The IonPac AS9-HC ion-exchange column was best suited for this analysis because of its ability to separate the ions of interest in less than 30 min with an isocratic carbonate-based eluent [7]. Under standard conditions with 9 mM sodium carbonate, chloride and carbonate coeluted. Increasing the eluent pH through the addition of sodium hydroxide resulted in stronger retention of carbonate. Consequently, chloride was baseline resolved and did not coelute with carbonate. A separation of an aqueous standard of, chloride, nitrate, sulfate and phosphate was determined with 8 mM sodium carbonate–1.5 mM sodium hydroxide at 0.25 ml/min, as shown in Fig. 4.

The IonPac AS9-HC used in this study showed an improvement over the IonPac AS10 used in the previous study [4]. The run time decreased from 35 min with the AS10 to less than 30 min with the AS9-HC. It was easier to prepare, preserve and suppress the carbonate-based eluent of the AS9-HC than the hydroxide eluent of the AS10. The AS9-HC had better resolution of chloride from the early eluting ions (fluoride, glycolate, acetate and formate) compared to the AS10.
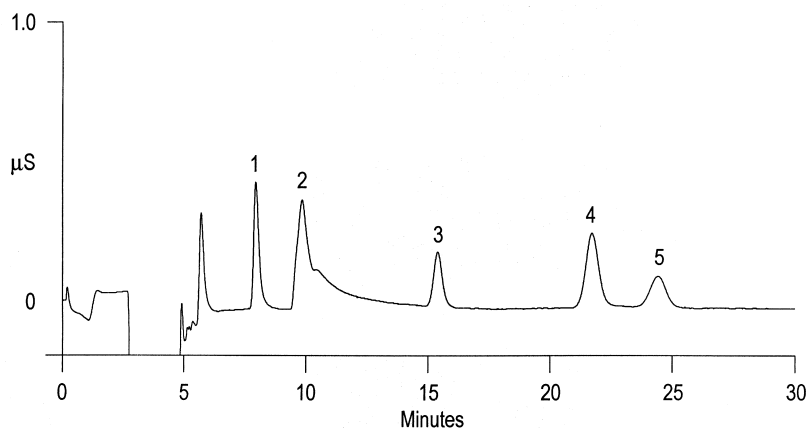

Fig. 4. Analysis of aqueous standard using the IC with matrix elimination procedure. Peaks: 1=chloride (1.00 μg/l); 2=carbonate, 3=nitrate (1.00 μg/l); 4=sulfate (1.00 μg/l); 5=phosphate (1.00 μg/l). Sample volume: 5 ml; analytical column IonPac AS9-HC (250×2 mm); guard column IonPac AG9-HC (50×2 mm); concentrator column AG9-HC (50×4 mm); detection: conductivity; suppression: ASRS, external water mode; eluent: 8.0 mM sodium carbonate–1.5 mM sodium hydroxide, isocratic; eluent flow-rate: 0.25 ml/min; rinsing reagent: deionized water; rinsing flow-rate: 2.0 ml/min.

An IonPac AG9-HC ion-exchange column was used as the concentrator column in the 50×4 mm format instead of 50×2 mm because the 4-mm column had four-times more capacity than the 2-mm column and lower back pressure at the microbore flow-rate. No significant degradation in separation efficiency was observed when coupling a 4-mm concentrator column with a 2-mm analytical column set.

A system blank was determined by using deionized water as the sample. The blank establishes baseline anion concentrations from such sources as the polyethylene sample container and the deionized

water. None of the anions of interest were detected in the blank. The blank can be was quantified by calibration standards prepared in deionized water.

Representative chromatograms of semiconductor-grade IPA "as received" and spiked with chloride, nitrate, sulfate and phosphate are shown in Fig. 5. The organic solvent and the amount of carbonate present in the sample can affect the response and retention time for the analytes of interest. A negative disturbance in the baseline was observed at 10 min for the unspiked IPA because it was deficient in carbonate relative to the amount in the eluent [13]. This negative disturbance was also observed for the
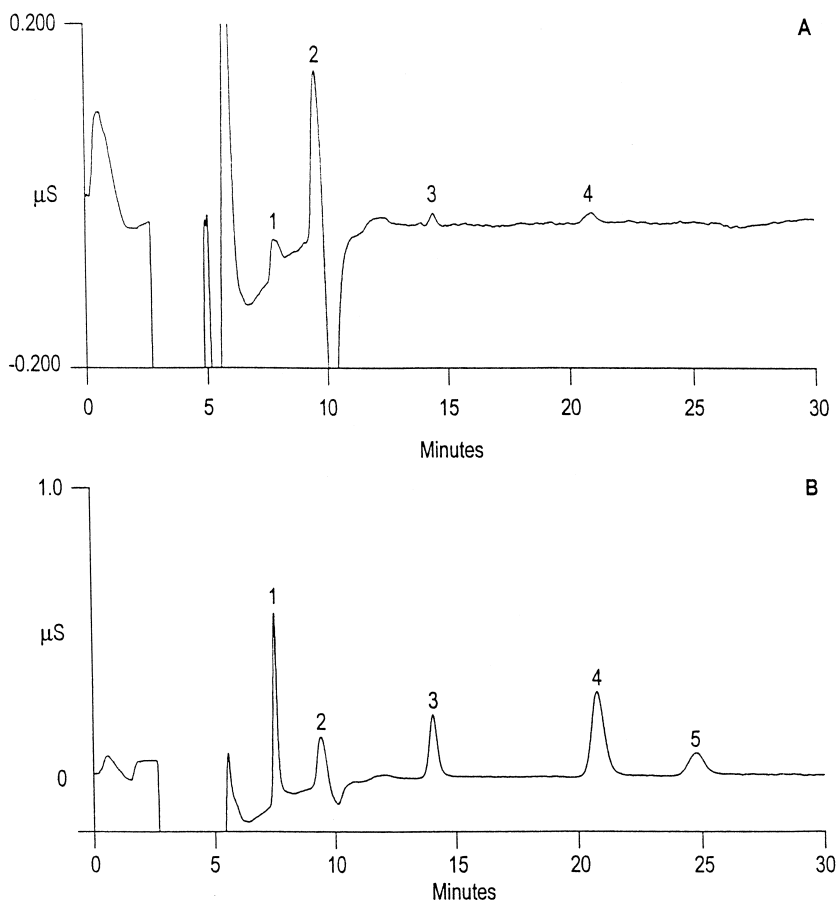
Fig. 5. Analysis of semiconductor-grade isopropanol by IC with matrix elimination. Samples: (A) unspiked 100% isopropanol and (B) spiked isopropanol (99% isopropanol and 1% aqueous standard). Peaks: (A) 1=chloride (0.538 μg/l); 2=carbonate, 3=nitrate (0.302 μg/l); 4=sulfate (0.164 μg/l) and (B) 1=chloride (5.18 μg/l); 2=carbonate, 3=nitrate (5.69 μg/l); 4=sulfate (4.60 μg/l); 5=phosphate (4.33 μg/l). Chromatographic conditions as in Fig. 4.

Table 3
Spike/recovery of trace anions in 99% isopropanol

Anion	IPA blank concentration (μg/l$\pm$SD, $n=5$)	Spike in IPA (μg/l)	Found – average blank (μg/l$\pm$SD, $n=5$)	Recovery (%)
Chloride	0.574$\pm$0.030	5.00	5.01$\pm$0.049	100
	0.546$\pm$0.029	5.00	4.39$\pm$0.27	88
Nitrate	0.551$\pm$0.130	5.00	5.62$\pm$0.29	112
	0.372$\pm$0.063	5.00	5.11$\pm$0.55	102
Sulfate	0.123$\pm$0.012	5.00	4.91$\pm$0.40	98
	0.145$\pm$0.024	5.00	4.17$\pm$0.35	83
Phosphate	<MDL[a]	5.00	4.74$\pm$0.32	95
	<MDL	5.00	4.28$\pm$0.33	84

[a] <MDL=Less than method detection limit.

99% IPA. However it was of less magnitude because of the carbonate present in the aqueous component of this sample.

The method of standard addition (adding one or more increments of a standard solution to sample aliquots of the same size) was used to quantify the anions of interest [14]. In this way we accounted for any effect of the sample matrix. Three different calibration standards prepared from different dilutions of the working standard were selected to bracket the expected concentrations in the samples. The concentrations were corrected by subtracting the

amount of the analytes of interest found in the deionized water blank. A summary of the recovery data for two spikes of 5.0 μg/l chloride, phosphate and sulfate in IPA is shown in Table 3. Recovery levels were determined to be between a target range of 75 to 125%.

This method was also evaluated with other high-purity, water-miscible organic solvents. Representative chromatograms for acetone and *N*-methylpyrrolidone (NMP) are shown in Figs. 6 and 7, respectively. Shifts in retention times observed for some of the later-eluting anions in these solvents
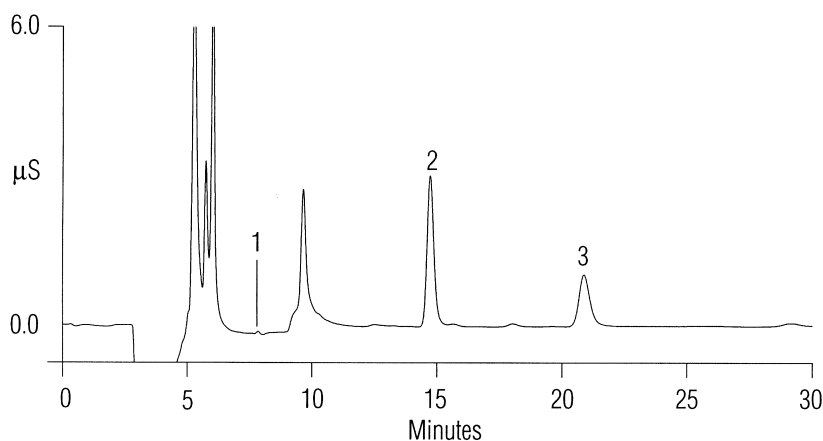

Fig. 6. Analysis of semiconductor-grade acetone by IC with matrix elimination. Sample: 100% acetone. Peaks: 1=chloride (0.01 μg/l); 2=nitrate (20 μg/l); 3=sulfate (5.5 μg/l). Chromatographic conditions as in Fig. 4.
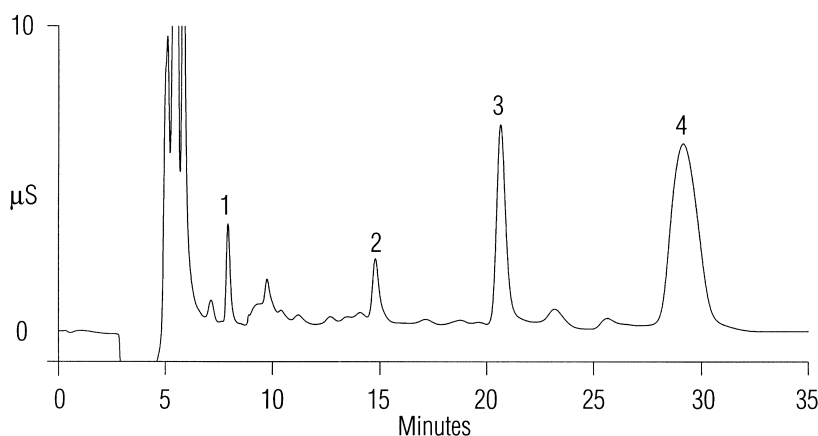
Fig. 7. Analysis of semiconductor-grade *N*-methylpyrrolidone by IC with matrix elimination. Sample: *N*-methylpyrrolidone. Peaks: 1=chloride (5.6 μg/l); 2=nitrate (13 μg/l); 3=sulfate (24 μg/l); 4=unidentified. Chromatographic conditions as in Fig. 4.

emphasize the importance of using the method of standard additions for quantification. NMP was found to have a higher level of contaminants than the IPA and acetone that were analyzed for this study.

A summary of the MDLs and Semiconductor Equipment and Materials International (SEMI) guidelines for maximum levels in IPA, acetone and NMP are presented in Table 4. MDLs were calculated using an ordinary least-squares regression analysis of the calibration data in the IPA matrix [16]. These values are an improvement over the previous work primarily because of the use of microbore (2-mm) analytical columns. The sensitivity of this method is substantially below the maximum limit of impurities as specified by SEMI for these reagents. To determine linearity of response for the analytes of interest, aqueous standards were

spiked into 99% IPA. Each of the four anions had a linear response with r^2 values greater than 0.99 from 1 to 10 μg/l. A summary of the regression data is shown in Table 5.

Table 5
Calibration[a] results for trace anions in 99% isopropanol

Anion	r^2	Slope ($\cdot 10^{-5}$)	Intercept
Chloride	0.9993	6.48±0.16	−0.598±0.155
Nitrate	0.9992	11.4±0.3	−1.17±0.182
Sulfate	0.9984	6.88±0.25	−2.10 ±0.276
Phosphate	0.9981	13.1 ±0.04	0.166±0.180

[a] Calibration curve based on linear regression for spiked concentrations of the analytes of interest prior to blank correction. Concentration levels: 1, 3 and 10 μg/l with three replicates at each level. Standard deviations are based on a 95% confidence interval.

Table 4
Method detection limits and SEMI specifications

Anion	Method detection limits[a] (μg/l)	IPA SEMI[b] Spec. C8.7-92 (μg/l)	Acetone SEMI[b] Spec. C1.2-96 (μg/l)	NMP SEMI[b] Spec. C8.9-94 (μg/l)
Chloride	0.592	50	200	300
Sulfate	0.758	50	–	250
Phosphate	0.754	50	100	250
Nitrate	0.647	50	–	400

[a] Method detection limit (MDL) based on an ordinary least-squares regression analysis in isopropanol matrix [15].
[b] SEMI=Semiconductor Equipment and Materials International [16].

4. Conclusion

Combined use of a 4-mm IonPac AG9-HC concentrator column and matrix elimination provide an improved analysis of anions in water-miscible organic solvents. Chloride, sulfate, phosphate and nitrate were determined to sub-μg/l levels with acceptable recovery. This technique can be very useful as a quality control test in many semiconductor applications and is applicable to water-miscible solvents that are compatible with the polymeric pathway in the IC instrumentation. Solvents that have been successfully used with this method include IPA, acetone and NMP.

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